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(54) **FILMS OU ARTICLES CREUX COMPRENANT UNE COUCHE DE POLYAMIDE**

(54) **FILMS OR HOLLOW ARTICLES CONTAINING A POLYAMIDE LAYER**

(57) Films monocouches ou multicouches, ou articles creux, comprenant au moins une couche de polyamide constituée de mica fluoré nano-dispersé. La présente invention porte aussi sur des emballages fabriqués à partir de ces produits, ainsi que sur les utilisations du polyamide renfermant du mica fluoré nano-dispersé pour produire des films ou des articles creux.

(57) This invention relates to single or multi-layer films or hollow articles containing at least one polyamide layer which contains nano-disperse fluorine mica, to packages produced therefrom and to the uses of polyamide filled with nano-disperse fluorine mica for the production of films or hollow articles.

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Films or hollow articles containing a polyamide layer

Abstract

This invention relates to single or multi-layer films or hollow articles containing at least one polyamide layer which contains nano-disperse fluorine mica, to packages produced therefrom and to the uses of polyamide filled with nano-disperse fluorine mica for the production of films or hollow articles.

Films or hollow articles containing a polyamide layer

This invention relates to single or multi-layer films or hollow articles containing at least one polyamide layer which contains nano-disperse fluorine mica, to packages produced therefrom and to the uses of polyamide filled with nano-disperse fluorine mica for the production of films or hollow articles.

Films and hollow articles which contain a polyamide layer exhibit many advantageous properties. Good optical properties may in particular be mentioned, such as elevated transparency in uncoloured films or hollow articles and elevated gloss. Good mechanical properties, such as elevated toughness, elevated puncture resistance, elevated tear propagation strength and others, are also significant. Moreover, production and further processing are, of course, simple.

Low permeability to oxygen, water vapour, carbon dioxide, fats, flavour substances and other essential components of the packaged goods or to substances which should be kept away from the packaged goods is of particular significance for many applications for films and hollow articles, in particular for use in the packaging sector.

In many cases, the stated requirements placed upon films or hollow articles are achieved by combining various materials in a multi-layer composite. In such a composite, the stated low permeability to oxygen is either achieved in part by the polyamide layer or layers of so-called high barrier materials are additionally used, such as for example polyvinylidene chloride or ethylene/vinyl alcohol copolymers (generally known by the abbreviation EVAL).

The use of high barrier layers has many disadvantages. Thus, the halogen content in the polyvinylidene chloride is frequently unwanted. Moreover, the high barrier materials are often expensive, difficult to obtain and exhibit disadvantages with regard to processability, such as for example low heat resistance.

When high barrier layers are dispensed with due to the stated disadvantages, low oxygen permeability of a multi-layer composite film or a multi-layer composite hollow article may, to a certain extent, be ensured by a polyamide layer. However, the oxygen barrier action of polyamide is frequently too low when it is used in a layer thickness such as is required to ensure adequate mechanical properties of a

multi-layer composite film or of a multi-layer composite hollow article. Using the polyamide in greater thicknesses solely to achieve an adequate oxygen barrier is generally prohibitively expensive.

EP-A 358 415 describes films made from polyamides which contain phyllosilicates and, by virtue of the phyllosilicate, have an increased oxygen barrier. However, it is only possible to incorporate the montmorillonite described in the Examples in EP-A 358 415 into the polyamide by means of a very elaborate process (montmorillonite must first be reacted with a swelling agent, such as for example an amino acid, before it can be incorporated into the polyamide).

EP-A 605 005 describes a composition prepared from polyamide and fluorine mica. Films of this moulding composition are not described. It is not usual to produce film from polyamides containing a mineral filler such as, for example, fluorine mica, because these films are generally not transparent, have low gloss and poor mechanical properties, such as for example low toughness.

The object thus arose of increasing the described excessively low oxygen barrier action of the polyamide by suitably modifying the polyamide, without impairing the other desired properties of the polyamide, in particular transparency, gloss or toughness. Moreover, it must be possible simply and cheaply to produce and process the modified polyamide.

It has surprisingly now been found that polyamides to which fluorine mica has been added as an additive achieve the stated object if the fluorine mica particles have a sufficiently small particle size. Polyamides provided with fluorine mica of a sufficiently small particle size exhibit reduced oxygen permeability, wherein the remaining advantageous properties of the polyamides, such as for example transparency, gloss and toughness, are adequately retained.

The present invention provides single or multi-layer films or hollow articles containing at least one polyamide layer, wherein the polyamide layer contains finely dispersed fluorine mica.

The present invention moreover provides the use of polyamide filled with nano-disperse fluorine mica for the production of single or multi-layer films or hollow articles.

The present invention furthermore provides packages made from a film according to the invention or from a hollow article according to the invention.

The finely dispersed fluorine mica in the polyamide layer is a fluorine mica of the formula (I)

$$x(MF) - y(aMgF_2 - bMgO) - zSiO_2$$

wherein

M denotes an alkali metal and the coefficients x, y, z, a and b have the following meaning:
$0.1 \leq x \leq 2$; $2 \leq y \leq 3.5$; $3 \leq z \leq 4$; $0 \leq a \leq 1$; $0 \leq b \leq 1$ and $a + b = 1$.

Preferably used fluorine micas of the above-stated formula are those in which M denotes sodium, lithium or potassium, wherein potassium is not used alone, but only in addition to lithium or sodium in a proportion by weight of up to a maximum of one third.

The average particle size of the fluorine mica present in the polyamide layer is less than 1 micrometre. The average particle size of the fluorine mica is preferably less than 100 nanometres. The average particle size of the fluorine mica is particularly preferably less than 50 nanometres. The particles generally have a size of at least 0.5 nm.

Average particle size is determined by visual inspection of transmitting electron micrographs of ultra-thin sections of the corresponding moulding compositions. In the event that the particles are highly anisotropic, particle size is taken to mean the dimension of the smallest axis (for example in the case of a lamellar particle, particle size is taken to mean the thickness of a lamella).

The fluorine micas are used in a concentration of 0.1 to 10 wt.%, relative to the total mass of the polyamide layer. The total mass of the polyamide layer is taken to mean the sum of the mass of the polyamide present in this layer and the mass of the fluorine mica present in this layer, together with the mass of further additives optionally present in this layer. The fluorine mica is preferably used in a

concentration of 0.5 to 5 wt.%. The fluorine mica is particularly preferably used in a concentration of 1 to 3 wt.%.

The polyamide present in the polyamide layer of the films or hollow articles according to the invention is a known aliphatic or aromatic or partially aromatic homopolyamide or copolyamide or a blend of two or more polyamides. Preferably used polyamides are polyamide 6 or polyamide 11 or polyamide 12 or polyamide 6,6 or polyamide 4,6 or polyamide 6,10 or a copolyamide prepared from units of the stated homopolyamides or a copolyamide prepared from caprolactam units and units derived from hexamethylenediamine and isophthalic acid or a copolyamide prepared from caprolactam units and units derived from isophoronediamine and isophthalic acid. Polyamide 6 or polyamide 6,6 or a copolyamide prepared from caprolactam units and units derived from hexamethylenediamine and adipic acid are particularly preferably used.

The fluorine mica used as a filler in the films or hollow articles according to the invention may be produced, for example, using the method described in US-P 5 204 078. The proportion of lithium hexafluorosilicate or sodium hexafluorosilicate, which is used together with talc in the production of the fluorine mica, is preferably 10 to 35 wt.% relative to the mixture of lithium hexafluorosilicate or sodium hexafluorosilicate and talc.

The films or hollow articles according to the invention may contain conventional quantities of further known auxiliary substances or additives. These further auxiliary substances or additives may be present in the polyamide layer which contains the stated fillers or also in other layers of the film.

The following may be mentioned by way of example of further auxiliary substances and additives: processing auxiliaries, such as for example lubricants, nucleating agents, stabilisers, anti-blocking agents, further fillers, fibrous or particulate reinforcing materials, such as for example glass fibres, glass beads or mineral fillers, impact modifiers, such as for example rubbers or polyolefins, flame retardants, dyes or pigments.

The films or hollow articles according to the invention may consist of only one polyamide layer or have a multi-layer structure. In the case of a multi-layer structure, the further layers may consist, for example, of polyolefins, such as for

example polyethylene or polyethylene copolymers, such as for example copolymers prepared from ethylene and acrylic acid or methacrylic acid or barrier polymers, such as for example polyvinylidene chloride or copolymers prepared from ethylene and vinyl alcohol (known as EVAL or EVOH).

The films or hollow articles according to the invention are produced in a known manner, for example by extrusion, coextrusion, coating, lamination or blow moulding. In the case of the films, extrusion or coextrusion may be performed, for example, using the so-called chill roll process or using the blown film extrusion process or blown film coextrusion process. In the case of multi-layer films or hollow articles, conventional commercial coupling agents may be used.

The raw material for the polyamide layers of the films or hollow articles according to the invention may be produced in a known manner using a continuous or discontinuous process. A discontinuous process may, for example, involve polymerisation in an autoclave. A continuous process may, for example, involve polymerisation in a so-called VK tube. Production is preferably performed using a continuous process. In order to achieve elevated molecular weights, as are frequently required for use as a film material, melt polymerisation may be followed by solid phase post-condensation. The fluorine mica may be added to the polyamide before, during or after polymerisation of the monomers to yield the polyamide. If the fluorine mica is added after polymerisation, it is preferably added to the polyamide melt in an extruder. If the fillers according to the invention are added before or during polymerisation, the polymerisation may include a temporally limited stage, during which polymerisation is performed in the presence of 1 to 50 wt.% of water. Introduction by polymerisation in the presence of such elevated quantities of water is the preferred production process.

The films or hollow articles according to the invention may be further worked or shaped before their ultimate intended use. The films according to the invention may thus, for example, be thermoformed.

In comparison with other films or hollow articles not containing the fillers according to the invention, the films or hollow articles according to the invention are distinguished by particularly low permeation values for oxygen and other gases and flavour substances. The other properties specific to polyamides, such as gloss, transparency and toughness are not impaired or only insignificantly so. The films

or hollow articles according to the invention may be produced and processed simply and at low cost using known processes.

The films or hollow articles according to the invention may be used, for example, for packaging purposes. Films or hollow articles according to the invention may be used, for example, for packaging foodstuffs, such as meat and meat products, sausage, cheese, beverages and the like. The films or hollow articles according to the invention may also be used, for example, for packaging cosmetics, such as sun protection creams or chemicals, such as plant protection products. The hollow articles according to the invention may moreover be used as pipes or tanks. These may be, for example, pipes or tanks for fuels or oils in motor vehicles.

Examples

Production of the filled polyamide used for film production:

7425 g of caprolactam, 1500 g of water and the quantity and type of filler stated in the particular Example are heated to 240°C for 2 hours in an autoclave under inherent pressure. The water is then vaporised at this temperature by reducing the pressure to atmospheric pressure. The resultant composition is then polymerised for 4 hours at 270°C. The resultant polyamide is extracted with water and dried.

Production of the films:

A 50 micrometre thick flat film is produced using the chill roll process (melt temperature: 260°C, casting roll temperature: 90°C) from the polyamide produced using the process described above.

Determination of filler particle size in the films examined:

The particle size of the fluorine mica in the polyamide film is determined by visual inspection of transmitting electron micrographs. In the event that the particles are highly anisotropic, particle size is taken to mean the dimension of the smallest axis (for example in the case of a lamellar particle, particle size is taken to mean the thickness of a lamella).

Example	Type of filler	Quantity of filler in g (wt.%)	Average particle size in nm	Relative solution viscosity of extracted polymer (1% in m-cresol, 25°C)
1 (Comparison)	no filler	-	-	4.3
2	fluorine mica	75 (1 wt.%)	9	4.3
3	fluorine mica	150 (2 wt.%)	9	4.3

Example	Oxygen permeation in (cm^3 × 25.4 µm) / (m^2 × 24 h × bar) at a relative humidity of the measuring gas of:			Tensile modulus to DIN 53 457 in MPa	Elongation at break to 53 455 in %	Gloss to DIN 67 530 in scale divisions	Haze to ASTM D 1003-61 in %
	25%	50%	75%				
1 (Comparison)	40	46	69	948	357	97	6.4
2	27	30	46	1370	200	67	2.5
3	20	23	33	1183	318	35	6.3

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A single or multi-layer film or hollow article containing at least one polyamide layer, wherein the polyamide layer contains finely dispersed fluorine mica.

2. A film or hollow article according to claim 1, wherein the polyamide layer contains 0.1 to 10 wt.% of fluorine mica, relative to the total mass.

3. A film or hollow article according to claim 1 or 2, wherein the average particle size of the fluorine mica is less than 1 micrometre.

4. A film or hollow article according to claim 1 or 2, wherein the average particle size of the fluorine mica is less than 100 nm.

5. A film or hollow article according to claim 4, wherein the average particle size of the fluorine mica is less than 50 nm.

6. A film or hollow article according to any one of claims 1 to 5, wherein the fluorine mica has the formula (I)

$$x(MF) \ -y(aMgF_2 \ -bMgO) \ -zSiO_2 \qquad (I)$$

wherein M denotes an alkali metal and the coefficients x, y, z, a and b have the following meaning:

$0.1 \leq x \leq 2$; $2 \leq y \leq 3.5$; $3 \leq z \leq 4$; $0 \leq a \leq 1$;
$0 \leq b \leq 1$ and $a + b = 1$.

7. A film or hollow article according to any one of claims 1 to 6, wherein the polyamide layer contains 0.5 to 5 wt.% of fluorine mica.

8. A film or hollow article according to claim 7, wherein the polyamide layer contains 1 to 3 wt.% of fluorine mica.

9. A use of a polyamide filled with finely dispersed fluorine mica according to any one of claims 1 to 8, for the production of a single or multi-layer film or hollow article.

10. A package comprising a film or a hollow article according to any one of claims 1 to 8.

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